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STOICHIOMETRY AND CHARACTERIZATION OF ALUMINUM OXYNITRIDE THIN FILMS BY ION-BEAM-ASSISTED PULSED LASER DEPOSITION (PREPRINT)

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14. ABSTRACT

Oxides are inherently stable in air at elevated temperatures and may serve as wear resistant matrices for solid lubricants. Aluminum oxide is a particularly good candidate for a matrix because it has good diffusion barrier properties and modest hardness. Most thin film deposition techniques that are used to grow alumina require high temperatures to impart crystallinity. Crystalline films are about twice as hard as amorphous ones. Unfortunately, the mechanical properties of most engineering steels are degraded at temperatures above 250 ~ 350 °C. This work is focused on using energetic reactive ion bombardment during simultaneous pulsed laser deposition to enhance film crystallization at low temperature.

Alumina films were grown at several background gas pressures and temperatures, with and without Ar ion bombardment. The films were nearly stoichiometric except for depositions in vacuum. Using nitrogen ion bombardment, nitrogen was incorporated into the films and formed the Al-O-N matrix. Nitrogen concentration could be controlled through selection of gas pressure and ion energy. Crystalline Al-O-N films were grown at 330 ºC with a negative bias voltage to the substrate, and showed improved hardness in comparison to amorphous films. Film deposition methodology and characterization of chemical and mechanical properties are reported in detail.

15. SUBJECT TERMS
Aluminum oxide, thin film deposition, crystallinity, ion bombardment, pulsed laser deposition, stoichiometric

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1. Introduction

Solid lubricants may be incorporated into hard coating matrices to protect them from oxidation while they lower friction and increase wear resistance across extreme environments. Most solid lubricants are relatively soft and are not abrasion resistant. This can reduce their operational lifetime through loss of material and generation of wear debris. A frequent shortcoming of solid lubricants is their inability to function well across a wide range of extreme environments. For example, MoS_2 provides a low friction coefficient and long life in vacuum/dry air, while graphite or diamond-like carbon (DLC) fails quickly. In comparison, graphite performs well in moist air, while the performance of MoS_2 is degraded. Both of these solid lubricants experience degraded performance above 400 ^{o}C because of oxidation and loss of the benefit H_2O molecules that provide in assisting lubrication by graphite.

To address these shortcomings, researchers have focused on developing oxide lubricants, oxythiomolybdates, additives, and composites [1-14]. Many of the oxides and the oxythiomolybdates are relatively soft and their room temperature performance is below that of MoS_2 and graphite. Additives have provided some promising results in increasing lifetime and lowering friction of MoS_2 in moist environments. Here, additives are defined as materials that are used to enhance the lubricant performance and whose purpose is not to provide a host matrix for the solid lubricant.

A different approach to extend life and increase performance is to incorporate the solid lubricant in a hard oxygen diffusion resistant matrix, where it is protected from abrasion and deep oxidation. The dispersed lubricant phase provides a reservoir that continuously supplies fresh lubricant as the wear process exposes new material,

replenishing oxidized or degraded surface layers. Using the matrix composite approach permits inclusion of several types of lubricants that can extend lubrication over a greater range of operational environments. NASA has developed several high temperature solid lubricant composite films by plasma spay techniques such as chromium carbide based PS212, chrome oxide based PS300, and nickel-chrome based PS304, where Ag and BaF_2/CaF_2 additives are used to provide lubrication at high temperatures [15-17]. Other composite systems have been reported including TiB_2/MoS_2, TiN/MoS_2, and Al_2O_3/MoS_2 [18-20]. Our efforts in matrix composite thin films have been focused on using DLC as a hard matrix, and as a good lubricant for terrestrial environments. TiC and WC were added as nano dispersions to toughen the films by restricting crack propagation. WS_2 was added to the WC/DLC film to increase performance in vacuum [21-25]. While these films have advanced the state-of-the-art in controlling friction across dry and moist environments, the matrices may oxidize or degrade at an elevated temperature. One approach for providing an oxidation resistant coating focused on yttria-stabilized zirconia with gold [26-30]. While this material system performed well, better matrices that are stable and good diffusion barriers are still required. Recently, YSZ-Ag-Mo nanocomposite films were produced that provided lubrication by forming a silver rich surface at 300-500 $^{\circ}$C and by oxide formation in friction contact at above 500 $^{\circ}$C [31-33]. A multilayer architecture of YSZ-Ag-Mo/ TiN, where TiN played diffusion barrier, was demonstrated to increase the film endurance and move toward thermal cycling capability.

The focus of this work was to develop alumina and aluminum oxynitride films as potential matrices for solid lubricants using low deposition temperatures. Al_2O_3 and AlON are oxidation resistant, good diffusion barriers and reasonably hard, but most films

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are amorphous as deposited by reactive magnetron sputtering [34-36]. The conditions used to grow crystalline alumina typically require a temperature in excess of 700 ^{o}C [37-39]. By increasing the degree of ionization during magnetron sputtering and accelerating those ions towards the substrate, crystalline alumina could be grown at a lower temperature. There were some studies at substrate temperatures between 400 to 500 ^{o}C that produced good films [40-43]. For our work, pulsed laser deposition (PLD) was used to ablate an alumina target and energetic Ar and N ions from a Kauffman ion source were used to add energy to the growing interface. Higher deposition rate, crystallinity and lower substrate temperature ($\leq$ 350 ^{o}C) were pursued by laser ablation in comparison to reactive magnetron sputtering. Stoichiometry and mechanical properties are specially discussed as they vary with nitrogen gas pressure and ion bombardment energy.

2. Experimental

2.1. Film deposition

A Lambda Physik COMPex 205 excimer laser was used to ablate a 99.99% pure hot pressed alumina target. The Ne-KrF gas mixture was used to provide 248 nm laser light. The laser beam pulse width was about 18 – 20 ns, and the pulse rate was 20 Hz. It was focused to a 2 mm by 4 mm rectangular area on the target face, providing a fluence of 3 J/cm^2. The beam hit the target at a 45˚ angle of incidence and was randomly scanned with a set of high-speed mirrors for minimizing local heating effects and ensuring uniform target erosion. Rotating the target and the substrate during deposition maximized film uniformity. The substrate holder was located 7 cm away from the target surface and could be internally heated and biased. Substrate temperature was controlled

within a 25 – 350 °C range based on calibrated pyrometer measurements. Additional details of the laser deposition system had been reported by Voevodin et al in an earlier publication [44]. A Kauffman ion source was aligned to bombard the substrate along its normal from a distance of 15 cm. The ion energy was varied from 100 to 800 eV and the ion flux was varied between 10^{15} to 10^{16} ions/cm^2. The base pressure in the deposition chamber was $5X10^{-9}$ Torr. Ar and N_2 partial pressures between 10^{-4} to 10^{-3} Torr were maintained by throttling a butterfly valve at the inlet to a turbo pump and by controlling flow rate up to 100 ~ 200 sccm. The films were deposited onto 25 mm diameter 440C steel disks, which were mirror polished (2 nm in R_a) prior to depositions. The films were grown to a thickness of 1 μm at a deposition rate of 1 μm per hour as measured by a calibrated quartz crystal oscillator.

2.2. Characterization

Film microstructure and chemistry were characterized by XRD and XPS. X-ray diffraction was performed using a Rigaku-D/max-1B diffractometer. Scans were collected in θ - 2θ mode with a Cu K_α x-ray source. Standard powder XRD patterns of body-centered cubic Fe and hexagonal $Al_{10}N_8O_3$ were used for data interpretation [45, 46]. Surface chemistry was studied using a Surface Instruments (SSI) M-probe XPS instrument operated at a base pressure of about $3X10^{-9}$ Torr. Using an Al anode plus monochromator and 25 eV pass energy, the full width at half maximum (FWHM) of the Au 4f$_{7/2}$ peak was 0.71 eV. Binding energy positions were calibrated against the Au 4f$_{7/2}$ peak and the energy separations were calibrated using the Cu 3s and Cu 2p$_{3/2}$ peaks at

122.39 and 932.47 eV, respectively. For samples that were charged, adventitious carbon at 284.5 eV was used as a reference.

2.3. Property testing

Film hardness was measured using a Nanoindentor IIs system equipped with a diamond tipped Berkovich indenter that was loaded to penetrate about 100 nm. Friction coefficients of the films were measured as approximate 0.5 using a ball-on-flat tribometer with the sample in the horizontal position. 6.35 mm diameter 440C steel bearing balls were used as the counterface. For each friction track, the rotational speed was adjusted to give a constant linear speed of 50 mm/s, and measurements were made at a normal load of 1 N. For the steel-on-steel case, this corresponds to a Hertzian contact pressure of 675 MPa. The relative humidity was maintained at $30\pm1\%$, and all friction measurements were made at room temperature.

3. Results and discussion

3.1. Alumina film investigations

The stoichiometry and hardness of alumina thin films grown by laser ablation of an alumina target in four different conditions are given in Table 1. Briefly, they were grown in vacuum, with oxygen, and with argon bombardment. The film grown in vacuum was moderately oxygen deficient. It is quite common to lose volatile species such as oxygen during PLD. In this instance, the oxygen atoms may recombine in the plasma or at the growing film interface and form O_2 molecules, which are pumped from the deposition system. This process competes with the formation of Al_2O_3. Addition of

5X10^{-3} Torr oxygen to the deposition environment increased the oxygen concentration in the films so that they were nearly stoichiometric. Nearly stoichiometric films were also grown by simultaneous growth using PLD and Ar ion bombardment at 300 V, 10^{-5} Torr Ar, and 10 sccm flow of Ar, which provided an ion flux of 10^{15} ions/cm^2. The Ar can assist in preventing oxygen atom recombination and cause dissociation and excitation of O$_2$ molecules in the deposition chamber. These circumstances increase the overall quantity of reactive oxygen for forming Al$_2$O$_3$. The chemical reactivity can be significantly increased by increasing temperatures. Nearly stoichiometric films were also grown on substrates at 300 ^{o}C in vacuum. Therefore, the chemistry can be properly controlled with oxygen reactant, Ar ion bombardment and high substrate temperature. Higher hardness was measured from the nearly stoichiometric films than the oxygen-deficient film, as demonstrated in Table 1. XRD measurements did not reveal any crystalline phase, and hence a higher substrate temperature would be required for crystallization. The result was in agreement with previous reports that the Al$_2$O$_3$ films grown by PLD were amorphous at low temperatures [47-50]. PLD depositions of alumina were the baseline of growing aluminum oxynitride films.

3.2. Aluminum oxynitride film investigations

Aluminum oxynitride thin films were grown using the combination of ion beam bombardment and PLD. Plasma plumes from laser ablation of an alumina target and nitrogen ion beams from a Kaufman source were intersected in the vicinity of substrates, where the reactive species of Al, N, O and NO were detected in the plasma. N and O atoms reacted with each other in the gas phase to form molecular NO [44]. The reaction

between arriving atomic Al and excited NO molecules on substrates resulted in the growth of Al-O-N films. Table 2 gives the different deposition conditions of ion beam energy and background gas pressure in the system. The films grown at 50 and 100 mTorr gas pressure showed pitting and/or holes in surfaces from depostion process, while flat uniform films were produced at 5 mTorr regardless of ion energy.

The film compositions of Al, O and N were measured using a XPS. The compositions in atomic percentage vary with gas pressure and ion beam energy and are shown in figures 1 and 2, respectively. At the constant ion energy of 300 eV, nitrogen content significantly decreased with increasing gas pressures from 5 to 100 mTorr. Oxygen content first went up and then decreased. The atomic percentage of Al remained nearly unchanged at approximate 40% with gas pressure. At the constant pressure of 5 mTorr, both the aluminum and nitrogen fractions went up with increasing ion energy, while oxygen content decreased. Therefore, the effect of high ion beam energy on the growth of Al-O-N films was different from the effect of high gas pressure in chamber. It should be noticed that an optimum Al_2O_3 crystal has 60 at.% of O and 40 at.% of Al in comparison to 33.33 at.% of O and N and 33.33 at.% of Al in a ternary AlON phase. The growth of Al-O-N films could be indicated by a significant increase of N and decrease of O, while the Al content was approximately same. Composition measurements suggested using a moderately low background pressure for Al-O-N depositions. The atomic ratio of N to Al in the films was studied in more detail in the low nitrogen pressure range of 0.6 to 15 mTorr, as shown in figure 3. The relative percentage of nitrogen increased at an accelerating rate as nitrogen pressure was reduced below 5 mTorr. Our spectroscopic measurements of plasma chemistries showed that decreasing the gas pressure resulted in

ion-beam-related plasma excitation zones close to the substrate [44]. The nitrogen ratio increased because there were more reactive species of nitrogen arriving on sample surfaces at a relatively low gas pressure.

XRD measurements showed a crystalline phase of Al-O-N when films were deposited at a substrate temperature of 330 ^{o}C, bias voltage of -200 V, background pressure of 1 mTorr, and ion beam energy of 300 eV. Figure 4 shows the XRD spectra from θ - 2θ scans of the films grown on steel substrates with and without a bias voltage. The film grown with no bias was amorphous and diffraction peaks were from the steel substrate, while a crystalline phase was present in the film grown on the biased substrate at -200 V. The characteristic XRD peaks are indicated by arrows in figure 4, which can be indexed according to the hexagonal $Al_{10}N_8O_3$ phase. The broad peaks with low intensity suggested that the film consisted of tiny/small crystallites embedded in an oxygen-rich amorphous matrix of Al-O-N because XPS measurements showed more oxygen than nitrogen in the film. A negative bias applied to the substrate during deposition additionally accelerated the positive ions from the plasma and resulted in crystallite growth.

Based on the stoichiometry and crystallization of Al-O-N films, hardness was measured for the films deposited at the substrate temperatures of 25, 330 and 350 ^{o}C, respectively, with and without a DC or RF bias voltage of -200 V, as shown in figure 5. The negative DC bias on the substrate helped to increase film hardness, while the RF bias did not. The Al-O-N films showed significantly higher hardness than the Al_2O_3 films grown at similar deposition conditions. The maximum hardness was exhibited by the Al-O-N film deposited at 350 ^{o}C and -200 V DC. The increase in arriving ion beam energy

and plasma excitation of both atomic and molecular species helped to create films with a fine crystalline structure, which may have increased film hardness via the Hall-Petch mechanism.

4. Conclusions

Al-O-N films were grown on steel substrates by combining the plasma plumes from laser ablation of an alumina target and nitrogen ion beam from a Kaufman ion source. For comparison studies, alumina films were also grown by PLD at several background pressures and substrate temperatures, with and without Ar ion bombardment. The nearly stoichiometric alumina films grown with Ar ion bombardment showed higher hardness than the oxygen-deficient film. The nitrogen content in the Al-O-N films increased with increasing ion bombardment energy, but decreased with increasing gas pressure. A negative bias voltage of -200 V DC to the substrate resulted in crystallization of the Al-O-N film at a moderate temperature of 330 $^{\circ}$C. Increase in the energy of arriving ions, plasma excitation and substrate temperature facilitated the growth of fine crystalline films. The film hardness was increased by incorporating nitrogen into the alumina film via heating substrate and increasing ion bombardment energy.

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Figure captions

Fig. 1. Atomic percentage variations of Al, O and N in the films as a function of pressure at a constant ion beam energy of 300 eV.

Fig. 2. Atomic percentage variations of Al, O and N in the films as a function of ion beam energy at a constant pressure of 5 mTorr.

Fig. 3. Relative percentage ratio of N to Al by the depositions in the low range of nitrogen gas pressure at 300 eV ion beam energy.

Fig. 4. X-ray diffraction spectra of the Al-O-N films grown with and without a negative bias voltage on steel substrates at 330 ^{o}C, 1 mTorr gas pressure and 300 eV ion beam energy.

Fig. 5. Hardness measurements of the Al_2O_3 and Al-O-N films deposited at substrate temperatures of 25, 330 and 350 ^{o}C with and without a DC or RF bias voltage of -200 V, respectively.

Table 1. Stoichiometry and hardness of alumina films grown at various deposition conditions

Deposition conditions	Stoichiometry	H GPa
Vacuum, RT	$Al_2O_{2.4}$	9.5 ± 1
5×10^{-3} Torr O_2, RT	$Al_2O_{2.9}$	11.0 ± 1
Ion Beam, RT	$Al_2O_{3.0}$	11.0 ± 1
Vacuum, 300°C	$Al_2O_{2.9}$	11.0 ± 1

Table 2. Al-O-N film deposition conditions including ion beam energy and background gas pressure used in the present studies

Ion energy (eV)	0	0	100	200	300	300	300	500	800
Pressure (mTorr)	5	50	5	5	5	50	100	5	5
Notes		SF				SF	SF		

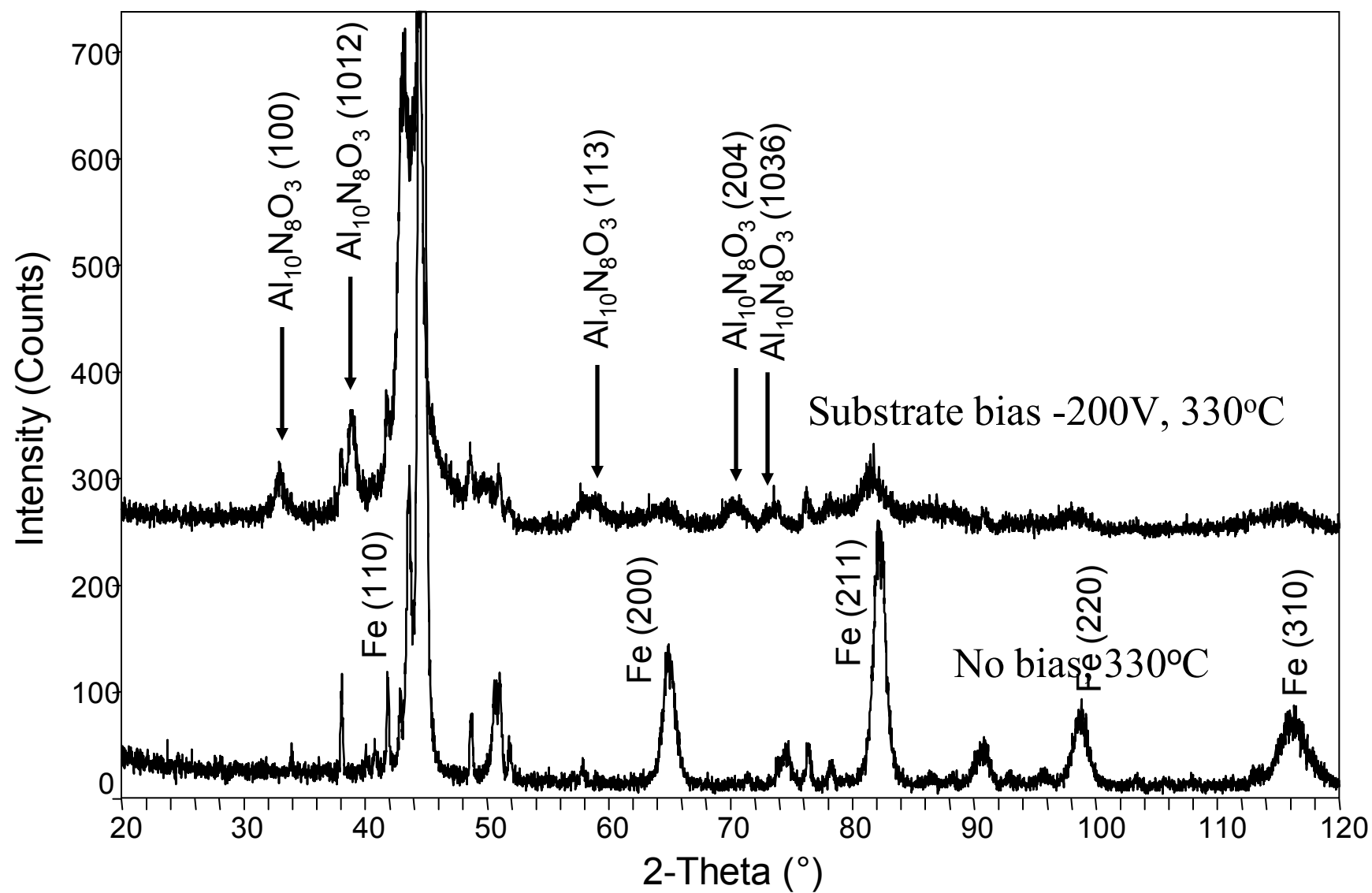*Surface features (SF): Pitting and/or holes in surface from deposition process

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5